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Pyrolysis of wheat straw-derived organosolv lignin

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ABSTRACT

The cost-effectiveness of a lignocellulose biorefinery may be improved by developing applications for lignin with a higher value than application as fuel. We have developed a pyrolysis based lignin biorefinery approach, called LIBRA, to transform lignin into phenolic bio-oil and biochar using bubbling fluidized bed reactor technology. The bio-oil is a potential source for value-added products that can replace petrochemical phenol in wood-adhesives, resins and polymer applications. The biochar can e.g. be used as a fuel, as soil-improver as solid bitumen additive and as a precursor for activated carbon.

In this paper we applied the pyrolysis-based LIBRA concept for the valorisation of wheat straw-derived organosolv lignin. First, we produced lignin with a high purity from two wheat straw varieties, using an organosolv fractionation approach. Subsequently, we converted these lignins into bio-oil and biochar by pyrolysis. For comparison purposes, we also tested two reference lignins, one from soda-pulping of a mixture of wheat straw and Sarkanda grass (Granit) and one from Alcell organosolv fractionation of hardwoods. Results indicate that ~80 wt% of the dry lignin can be converted into bio-oil (with a yield of 40–60%) and biochar (30–40%). The bio-oil contains 25–40 wt% (based on the dry lignin weight) of a phenolic fraction constituting of monomeric (7–11%) and oligomeric (14–24%) components. The monomeric phenols consist of guaiacols, syringols, alkyl phenols, and catechols. 4-vinylguaiacol is the major phenolic monomer that is formed during the pyrolysis of the straw lignins in yields from 0.5–1 wt%. For the hardwood-lignin Alcell, the predominant phenol is 4-methylsyringol (1.2 wt%). The ratio guaiacols/syringols seems to be an indicative marker for the source of the lignin.

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1. Introduction

1.1. Background

The increasing use of fossil fuels is associated with global problems such as climate change, environmental pollution, and security of supply. This has led to a renewed interest in the use of renewable sources such as sun, wind, hydropower, and biomass for energy and materials. Lignocellulosic biomass can be used as a renewable feedstock for the co-production of materials, energy, chemicals, and (transportation) fuels via integral biorefinery concepts [1]. To date, no commercial lignocellulosic-based biorefineries exist. The few existing pilot plants merely focus on the production of bioethanol. Residual streams are either disposed of, used as filler in cattle feed or combusted for heat and power generation.

1.2. Biomass composition; structure of lignin

Lignocellulosic biomass is a composite biopolymer of intertwined cellulose (35–45% dry weight basis), hemicellulose (25–30%

dry weight basis) and lignin (20–35% dry weight basis). Lignin is an amorphous polymer consisting of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), *p*-coumaryl, coniferyl and sinapyl alcohol (Fig. 1). The highly cross-linked phenolic substructures that originate from these monolignols are called *p*-hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapyl alcohol) moieties [2]. During the biological lignification process, the monolignols form a complex three-dimensional amorphous polymer that contains a great variety of bonds with typically around 50% β-O-4 ether linkages.

Softwood lignins mainly contain guaiacyl units, while hardwood lignins contain both guaiacyl and syringyl units. All three monolignols H, G, and S occur in the lignin from herbaceous plants in significant amounts. Lignin is associated with hemicellulose via covalent bonds. Hemicellulose presumably provides the interconnection between cellulose and lignin [3]. Based on its chemical structure, lignin is a potentially valuable source of aromatic chemicals [4,5].

1.3. Wheat straw lignin

Wheat straw is an abundant agricultural residue from the production of cereals. The global production of wheat straw is

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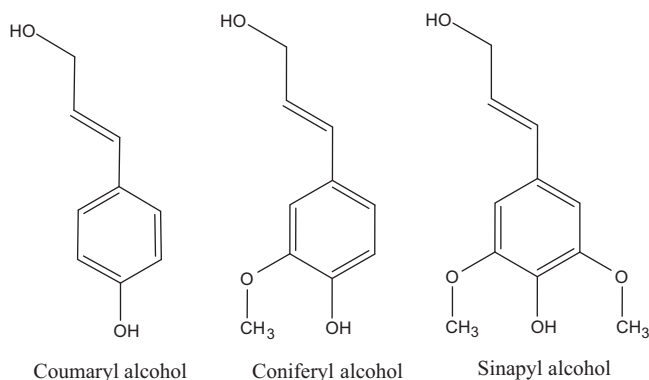


Fig. 1. Lignin monolignols.

approximately 529 million tonnes per year, mainly from Asia (43%), Europe (32%) and North America (15%) [2]. Wheat straw is an attractive low-cost feedstock for the production of bioethanol because of its annual renewability and abundance. Wheat straw lignin is a *p*-hydroxyphenyl–guaiacyl–syringyl (H–G–S) lignin and contains all of the three monolignols in significant quantities, typically 5% H, 49% G and 46% S [2].

1.4. Lignin valorisation in a biorefinery

Lignin is a major (future) residual stream from both the pulp- and paper industry and from 2nd generation biorefineries producing chemicals and biofuels such as bioethanol. Despite its potential as a renewable source for aromatic chemicals, industrial valorisation processes for lignin are rare. However, valorisation of lignin will be the key issue in the further development of lignocellulosic biorefineries for fuels and/or chemicals. Conversion of lignin to chemical feedstocks will positively influence the economic viability resulting in a substantial decrease of the production costs of biofuels such as bioethanol and other chemicals. Fig. 2 presents an example of a scheme of a multi-product biorefinery including lignin upgrading [6].

1.5. Primary biorefinery (organosolv fractionation)

For an effective production of chemicals, the lignocellulosic biomass has to be fractionated into its three main constituents to overcome its structural and compositional heterogeneity and complexity. Traditionally, the pulp- and paper industry uses various

biomass pulping processes such as Kraft pulping to isolate the cellulose fibres for the production of paper. However, during these processes the hemicellulose and lignin fractions are degraded, limiting their valorisation possibilities.

Second generation biorefineries for the production of bioethanol use pre-treatment technologies to make the (hemi)cellulose accessible for (enzymatic) hydrolysis [7]. Unfortunately, in most pre-treatment processes, lignin ends up in a residue together with non-hydrolyzed sugar polymers, feedstock minerals, and process chemicals. This type of residue seems only suited as fuel for heat and power generation. An alternative pretreatment technology is organosolv fractionation that uses organic solvents such as ethanol to delignify biomass prior to enzymatic hydrolysis [8,9]. Subsequently, the lignin can be recovered from the organosolv liquor with a high purity and essentially free of sulphur and ash. These lignin characteristics will facilitate valorisation of lignin into products like resins and phenol(ics).

1.6. Secondary biorefinery (lignin pyrolysis)

Lignin is a thermoplastic material and shows considerable recalcitrance towards thermal depolymerisation, e.g. via pyrolysis (thermal degradation of organic matter in absence of air). The literature on the pyrolysis of lignin for the production of chemicals typically reports yields of mono-phenolic compounds that rarely exceed 5–6%, based on lignin [10–12]. Economic and technological considerations still preclude a large-scale mass production of low molecular weight chemicals from lignin in competition with petrochemicals. This is inherent to the specific nature of the complex and stable lignin polymer, that makes it difficult to convert it into valuable monomeric chemicals.

Earlier work on the pyrolysis of beech wood-derived organosolv lignin already reported the difficulties of feeding the lignin to a fluidised bed reactor [13].

The beech wood lignin was fed in the reactor zone by means of dropping it on top of the bubbling fluidized bed in the reactor in the form of pre-shaped pellets because it appeared to be impossible to feed the original lignin with conventional screw-feeding technology. In addition, in a recent international collaboration it was attempted to carry out fast pyrolysis of a pure lignin and analyze the products in order to firstly establish the potential for this method of lignin processing and secondly to compare procedures and results [14]. The research was carried out in the IEA Bioenergy Agreement Pyrolysis Task 34–PyNe. Due to melting phenomena during feeding and subsequent agglomeration and bed-defluidisation in the pyrolysis reactor, the lignin was difficult/impossible to process and it

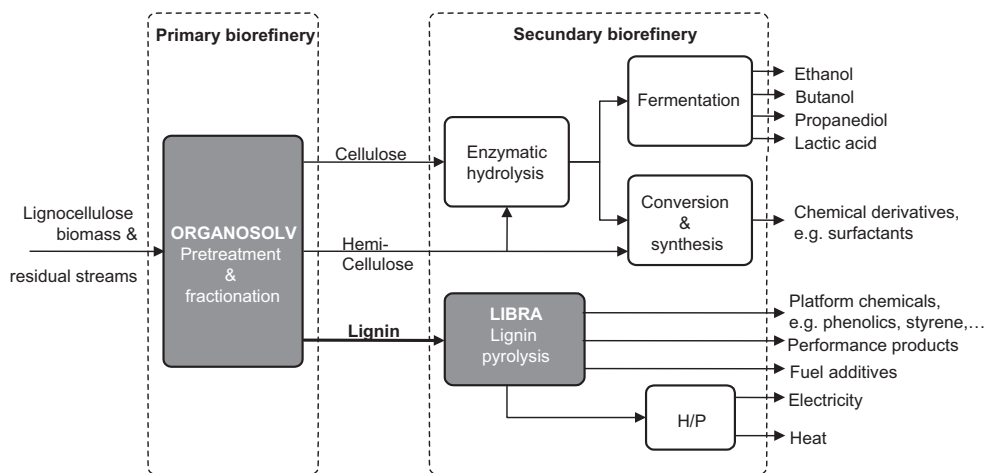


Fig. 2. Lignin valorisation in a multi-product lignocellulose biorefinery [6].

turned out that lignin cannot be effectively fast pyrolysed in reactor systems designed for whole biomass materials [14].

Therefore, we have developed LIBRA, a new Lignin BioRefinery Approach, based on bubbling fluidised bed pyrolysis technology [15] to thermochemically convert pure lignins in a phenolic bio-oil and biochar. The pyrolysis technology is capable of continuously processing pure lignins via a combination of specially designed cooled-screw feeding technology with co-feeding a proprietary catalyst.

The resulting biochar can be applied as fuel to generate heat for the pyrolysis process. Other applications might be its use as soil improver [16] and as precursor for activated carbon [17]. The phenolic bio-oil can substitute phenol in wood resins and is a possible substitute or modifier for petrochemical bitumen. In addition, the phenolic oil is a source of phenols for pharmaceutical, food, and other fine chemical applications.

Fig. 3 illustrates and summarizes the integrated approach of production and subsequent pyrolysing of lignin that we have followed.

1.7. Pyrolysis of wheat straw-derived organosolv lignin

In this paper we present an innovative integrated biorefinery approach that has the potential for a full valorisation of wheat straw, an abundant agro-residue, into value-added products via an efficient fractionation and subsequent (thermo) chemical processing of the main fractions hemicellulose, cellulose and lignin. The focus of the work in this paper is the pyrolytic valorisation of the straw-derived lignin residue. We describe bubbling fluidized bed pyrolysis experiments with wheat straw-derived organosolv lignins. For comparison purposes the pyrolysis results of two commercially available technical lignins are discussed as well.

2. Materials and methods

2.1. Feedstocks

2.1.1. Wheat straws

Two varieties of wheat straw were used as feedstock for the production of lignin, Dutch winter wheat straw (wheat straw A) and Spanish wheat straw from the region around Salamanca (wheat straw B). Both wheat straw batches were received ambient-dry, cut into pieces <2 cm, and were stored at room temperature in a closed vessel. A representative sample was taken for the organosolv experiments and used without further treatment. The composition of both wheat straws is given in Table 1.

2.1.2. Reference lignins

For comparison purposes two reference lignins were used; (1) Alcell lignin: a deciduous lignin prepared in the 1980s by Repap Technologies (now Lignol) via the Alcell organosolv process from a mixture of hardwoods and (2) Granit lignin: a herbaceous lignin produced by Asian Lignin Manufacturing (ALM) from soda-pulping of annual non-woody plants like wheat straw and Sarkanda grass (*Saccharum munja*). Granit lignin is today marketed by Granit SA (now GreenValue), Switzerland.

2.2. Lignin production by organosolv fractionation

Organosolv experiments were performed in 2 L and 20 L autoclave reactors (Kiloclave, Büchi Glas Uster AG, Switzerland). Wheat straw was mixed with the solvent (60%, w/w aqueous ethanol) in a ratio of 10 L/kg dry biomass and the slurry was heated to the reaction temperature (200 °C) while being mixed. Subsequently, the reactor was kept isothermal during the reaction time (60 min) and cooled down to below 40 °C.

After organosolv treatment, the product suspension was filtered quantitatively over a Whatman type 3 paper-filter. The filtrate or “organosolv liquor” was stored in a refrigerator for lignin recovery. The solid fraction remaining after organosolv was washed with 60% (w/w) aqueous ethanol in similar amount as the solvent applied in the organosolv process itself. The resulting washing liquor was also stored in a refrigerator for lignin recovery.

Lignin was precipitated from the organosolv liquor and the washing solution upon dilution with refrigerated water (water: solution 3:1, w/w). The resulting mixture was left at room temperature for at least 30 min until the lignin particles floated on top of the solution. After sedimentation of the particles by centrifugation, the supernatant was decanted and the lignin was dried and weighted. The lignins produced were not washed.

Process set-up used to produce the different lignin batches and the obtained results are given in Table 2.

2.3. Lignin characterization

2.3.1. Composition

The moisture and ash content of the lignin samples were measured according to the protocols NREL/TP-510-42621 and 42622, respectively [19]. The summative compositional analysis (i.e., contents of lignin, carbohydrates) of the lignins samples was determined in duplicate by using a modified hydrolysis protocol based on TAPPI methods T 222 and 249 [20] and the NREL protocols [19,26]. No extractions were performed prior to hydrolysis. For more details about these analyses we refer to [9]. The elemental analysis (C, H, N, O) of the lignins was determined in duplicate using a Carlo-Erba analyzer.

2.3.2. Thermal characteristics

Lignins A and B were characterized by thermogravimetric analysis (TGA) under N₂ with a Mettler Toledo TGA 850 featuring automated temperature and weight control and data acquisition. After loading the aluminum oxide sample holder with approx. 10 mg of lignin, the sample was kept at room temperature for 15 min. Subsequently the lignin was heated to 100 °C with 5 K/min, followed by an isothermal drying period of 15 min at 100 °C. After drying the sample was further heated to 500 °C with 10 K/min to measure its thermal degradation behavior as function of temperature. Finally, the sample was cooled down to room temperature again. Throughout the experiment, the sample was kept under 20 ml/min of nitrogen gas.

A blank experiment (no lignin sample) was conducted to calibrate the equipment. TGA analysis results on the two reference lignins Alcell and Granit have been reported previously [15].

2.3.3. Molecular weight distribution

All lignins were subjected to a size exclusion chromatography (SEC) analysis to determine their molecular weight distribution. The HP-SEC protocol as described by Baumberger et al. and Goselink et al. [21,22] was followed using 0.5 M NaOH. The major modification made was an elution temperature of 40 °C instead of room temperature.

2.4. Pyrolysis experiments and product analysis

Batch experiments were conducted using an atmospheric pressure, 1 kg/h (maximum solid feed rate) bubbling fluidized bed test facility at 500 °C (Fig. 4) featuring fully automated operation and data acquisition (pressure, temperature, permanent gases). The hot sand bed was fluidized with argon at approximately five times the minimum fluidization velocity. Each batch pyrolysis experiment was started with the feeding of approximately 40 g ambient-dry lignin particles to the reactor at a solid feed rate of 500 g/h. The

Table 1
Summative compositional analysis wheat straw raw materials. Results are in % w/w of the dry biomass.

Raw material	Extractives		Lignin		Arabi- nan	Xylan	Mannan	Galac- tan	Glucan	Ash	Total
	H ₂ O	EtOH	AIL	ASL							
Wheat straw A [18] ^a	8.4	2.0	16.7	1.1	1.9	19.9	0.2	0.7	36.9	6.1	93.8
Wheat straw B [9] ^b	11.2	2.0	15.1	1.0	2.1	21.5	0.2	0.5	34.6	8.5	96.9

^a Elemental composition wheat straw A [18]: C 44.3; O 42.7; H 5.4; Si 2.2; K 0.3; N 0.3; Ca, 0.2% (w/w), dry biomass.
^b Wheat straw B [9]: C 43.8; O 41.7; H 5.4; Si 2.4; K 1.4; Cl 0.5; N 0.2; Ca, 0.2 (other elements <0.1) (w/w), dry biomass.

Table 2
Process set-up and results for the production of lignin from wheat straw.

Lignin sample	Biomass	Organosolv set-up and operational mode		Pulp yield (% w/w, dry biomass)	Lignin yield (% w/w) ^a
		Reactor vessel (L)	Liquor recycling ^b		
A	Wheat straw A	20	No	61	67
B	Wheat straw B	2	Yes	60	86

^a Lignin yield calculated based on lignin content in dry biomass.
^b In the recycle set-up, a batch of raw material was pulped in the organosolv liquor resulting from the previous experiment. For the first experiment and make-up of solvent losses, fresh aqueous ethanol was used. Lignin was precipitated from the concentrated liquor obtained from the final experiment (and the washing liquor of each individual experiment).

lignins were co-fed with a proprietary catalyst as 1–3 mm particles using a specially designed hollow water-cooled feed screw in order to suppress melting during feeding. After the concentration of the permanent gases CO, CO₂ and CH₄ and aerosols was observed to decrease to approximately the starting values, the experiments were deliberately stopped, typically 20–40 min after the time that feeding and sampling commenced.

The pyrolysis products were sampled directly above the fluidized bed to ensure a short residence time of the vapors in the hot reactor zone, typically 1–3 s. Sampling took place using a slightly adapted protocol to collect biomass gasification/pyrolysis tars [23]. After filtration of the entrained char particles in a heated soxhlet filter, the pyrolysis vapors and aerosols passed through a series of seven impingers filled with isopropyl alcohol as quenching solvent (see Fig. 4). Isopropylalcohol (2-propanol) is well known as a solvent for relatively non-polar compounds. Due to the low sampling temperature (around 0 °C) it is expected that the IPA does not significantly react with the incoming pyrolysis vapors. In addition, the excess amount of IPA (when compared to the sampled amount of

pyrolysis products) directly dilutes the vapor components, thereby minimizing secondary reactions between the reactive pyrolysis products. After the experiments the contents of the IPA-impingers were collected in a dark glass bottle that was immediately placed in a refrigerator at 4 °C to prevent secondary reactions.

Liquid and gaseous products were analyzed using standard chemical analysis methods. Most organics were measured off-line with a TRACE-GC-ULTRA GC/MS, equipped with a polar wax column and a DSQ-II mass spectrometer. GC-undetectable species such as oligomeric lignin degradation fragments were determined gravimetrically after evaporation of a part of the collected IPA sample at room temperature under air till constant weight.

The amount of pyrolysis products was calculated from the measured concentrations of organics and water in the IPA sample, the total amount of the IPA sample and the ratio (total product gas flow rate): (sampling flow rate). During sampling, only a fraction of the total product gas flow was collected. In the calculations, the total product gas flow rate is assumed to be equal to the fluidization flow rate. Actually, the total gas flow in the conducted pyrolysis

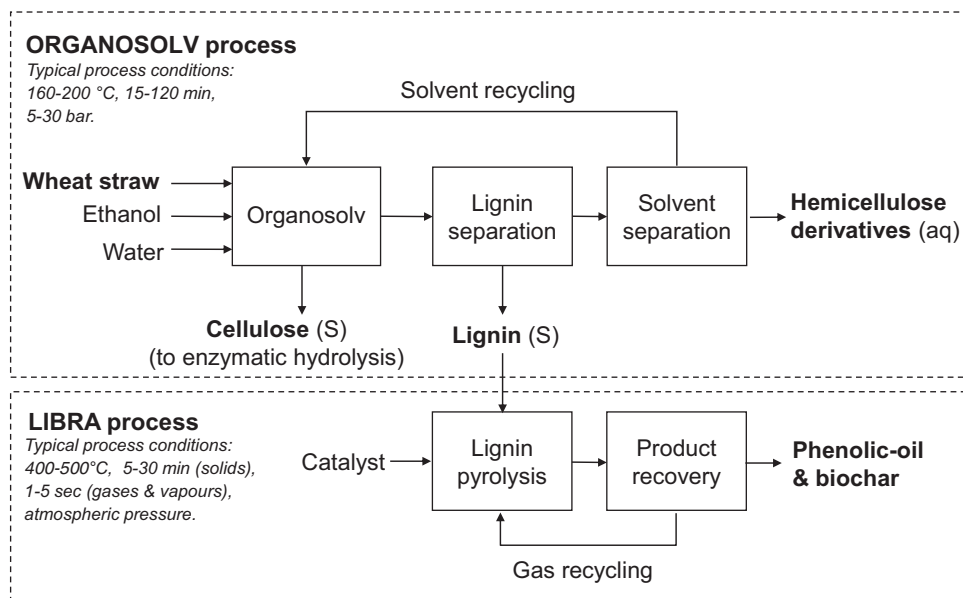


Fig. 3. Combination organosolv fractionation – lignin pyrolysis for full valorisation of wheat straw into cellulose, hemicellulose derivatives and lignin for phenolics and biochar.

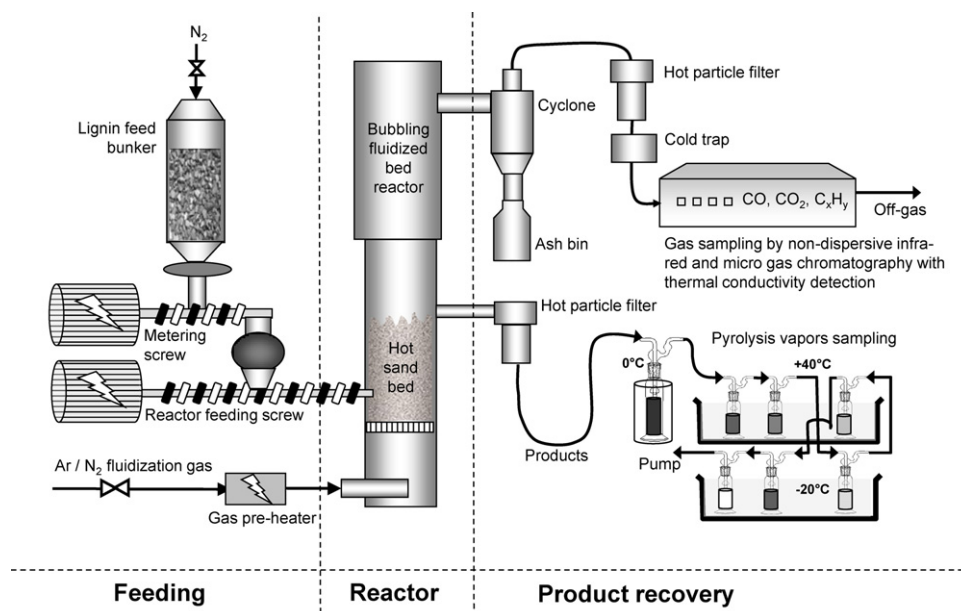


Fig. 4. Experimental set-up for the lignin pyrolysis tests.

experiments is somewhat larger than the fluidization gas flow because of the liberation of gaseous components from the pyrolysing biomass. However, the amount of gas that is formed during the pyrolysis is small, because of the small solid feed rate of biomass compared to the weight of the hot sand bed. The average contribution of the main non-condensable pyrolysis gases to the total gas flow has been estimated to be in the order of 1% of the fluidization gas flow (20 Nl/min). In the calculation of the final product yields, this small contribution has been neglected.

NDIR spectrometry (ABB-Advance Optima, CALDOS-MAGNOS) was used for on-line monitoring of CO, CO₂ and CH₄. Higher volatile organics such as ethane, ethylene, benzene and toluene were measured on-line with a Varian, CP4900 microGC by injection of a product gas sample on separate columns (Poraplot PPU for ethane, ethylene and acetylene) and CP-Wax 52CB for benzene, toluene and xylenes) with detection via a thermal conductivity detector. In general, the gas concentrations of these components were well below 0.1 vol%. Occasionally, the concentration of ethylene was around

0.2 vol%. Because of these low values and the overall experimental uncertainty (~10%) these gases were not taken into account for the calculation of the mass balances.

Karl-Fischer titration was applied to analyze the water content in the liquid organic samples.

Further details on the experimental procedure can be found in our earlier work [15].

3. Results and discussion

3.1. Lignin characterization

3.1.1. Composition

Table 3 presents the results of the elemental and summative compositional analysis of the lignins A, B and Alcell. The data for the Granit lignin have been taken from the literature [24]. The analysis of the lignins revealed that all tested lignins are similar in composition. They are more than 90% pure and contain a low

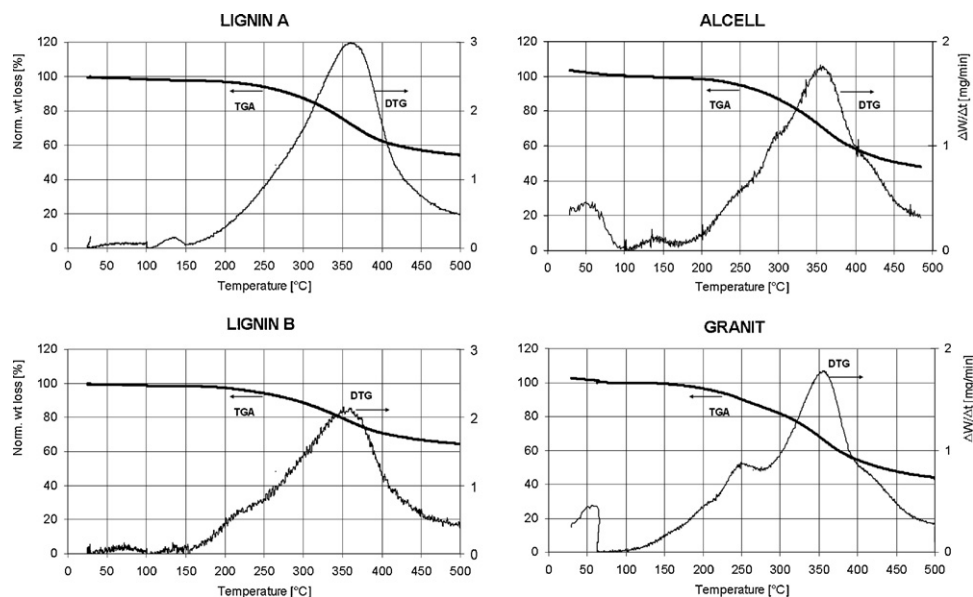


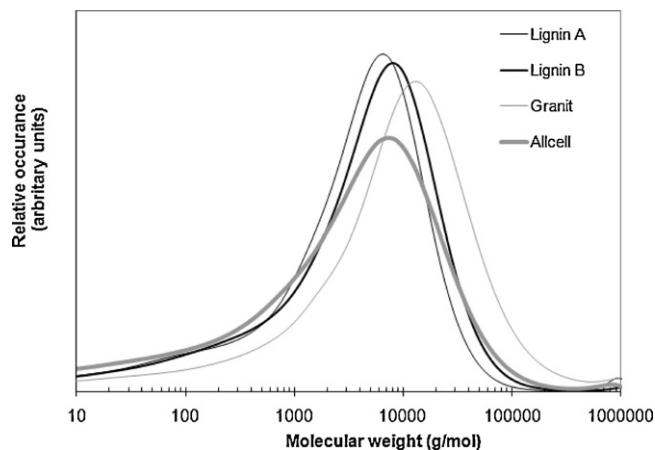
Fig. 5. Thermal characterization results for lignins A, B, Alcell [15] and Granit [15].

Table 3

Composition of lignin samples. Results are in % (w/w) of dry lignin.

Lignin Sample	Elemental				Chemical						
	C	H	N	O	AIL	ASL	Lignin	Glucan	Xylan	Carbohydrates	Ash
A	63.0	6.0	1.0	26.2	94.8	1.5	96.4	0.2	0.4	0.7	0.0
B	62.3	6.2	0.6	27.6	92.7	2.2	94.8	0.3	0.2	0.5	0.1
Granit	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	>90	n.a.	n.a.	<5	<2
Alcell	63.9	6.1	0.2	27.4	93.8	1.9	95.7	0.0	0.1	0.1	0.0

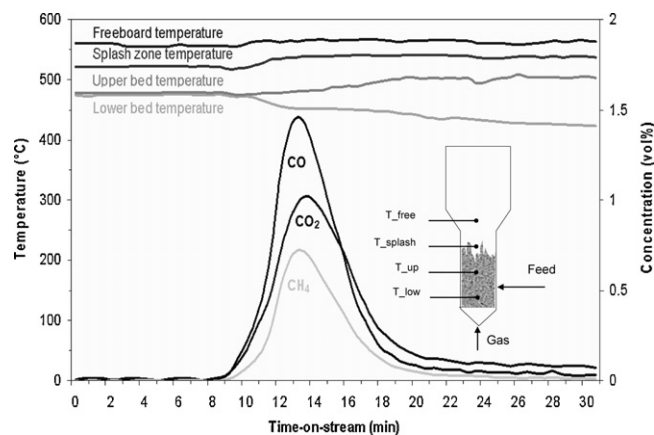
n.a., not available.

**Fig. 6.** SEC molecular weight distribution lignins.

amount of ash. The content of residual carbohydrates is for A, B and Alcell well below 1 wt% with Alcell containing the lowest amount of 0.1 wt% xylan. The contamination of the Granit lignin with carbohydrates is less than 5 wt%. This implies that the Granit may well contain some residual carbohydrates in contrast to the organosolv lignins. Except for nitrogen, the results of the elemental analysis are quite similar for the tested lignins. The differences in the N-content can be attributed to the different biomass feeds. In general, hardwoods contain less nitrogen containing material such as proteins than herbaceous biomass types.

3.1.2. Thermal characteristics

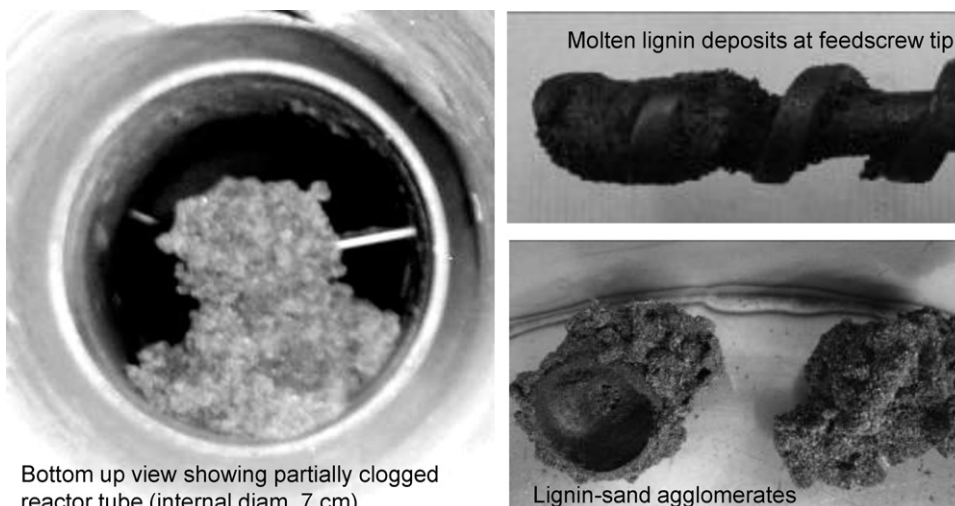
Figure 5 presents the TGA/DTG curves for the tested lignins. TGA analysis of lignins A and B shows a maximum thermal degradation around 365 °C. The main weight loss starts at 150 °C. It levels off

**Fig. 7.** Temperatures and gases from the pyrolysis of lignin A at 500 °C.

at 500 °C leaving behind a residual weight of 50–60% of the original amount. The final residue is the char that remains when all the volatile matter has been released. The TGA results for lignins A and B are comparable to the results that were obtained with Alcell and Granit [15]. The major difference is the low-temperature shoulder in the DTG curve of the Granit lignin around 250 °C. This shoulder is not present in the DTG curves of the organosolv lignins. It is possible that this low-temperature shoulder arises from the decomposition of residual carbohydrates from hemicellulose. From the thermal characterization results a temperature of 400–500 °C was considered to be suitable for the subsequent pyrolysis trials.

3.1.3. Molecular weight distribution

The molecular weight distributions of the investigated lignins determined by size exclusion chromatography (SEC) are presented in Fig. 6. Results presented mainly have a relative value, since the

**Fig. 8.** Clogged reactor tube, char-sand agglomerates and molten lignin at the tip of the feed-screw.

absolute molecular weight of lignins determined by SEC are known to be set-up specific [22]. Molecular weight determination by SEC is dependent on many practical aspects including material and way of packing of the columns.

This implies that only results obtained under the same operational conditions within the same laboratory using the same equipment can be compared with confidence. The molecular weight maxima increase in the order lignin A, lignin B, Alcell lignin, and Granit lignin. The figure also indicates a broader molecular weight range for Alcell and Granit compared to lignins A and B.

3.2. Lignin pyrolysis

3.2.1. Bubbling fluidized bed pyrolysis experiments

Fig. 7 graphically illustrates a typical course of a pyrolysis experiment, in this case for lignin A. Reactor temperatures and evolved gas concentrations are plotted as function of time on stream.

Lignin A was fed as a mixture of particles with an average size of 2 mm. Fig. 7 clearly shows that approximately 5 min after feeding started, the axial temperature profile in the reactor bed drastically changes. Simultaneously with the formation of the permanent gases, an axial temperature gradient of $>50^{\circ}\text{C}$ develops. This typically indicates bed-agglomeration and/or bed-defluidisation. Indeed, after the experiment the reactor tube appeared to be partially clogged with char-sand agglomerates that were also observed in the bed material. In addition, the tip of the feed screw contained some molten lignin deposits (see Fig. 8). After the experiment, a small amount of unreacted lignin powder was recovered from the feeding screw tube. Apparently, lignin powder is heated up more quickly and – as a consequence – melts more easily than the bigger particles. Therefore, during the other experiments it was ensured that the feedstock contained only lignin particles with a minimal amount of powder. As a result, no significant agglomeration was observed anymore.

3.2.2. Product yields

Table 4 presents the results of the pyrolysis experiments with the four lignins. From Table 4 it can be seen that the mass balances are close to 100%. The main uncertainty is the amount of char and the amount of oligomeric substances in the liquid that are difficult to determine. The amount of oligomers are estimated gravimetrically after evaporation of the primary product mixture (trapped components in isopropanol) until a constant weight is attained. The residual weight is corrected for the loss of the volatile components. This amount is uncertain because some volatile species might still be present in the residue. As a consequence, the amount of oligomers is probably slightly overestimated.

The amount of char is uncertain because of possible losses during the experiment (incomplete collection due to cyclone/filter slip-through) and due to handling afterwards (removal of the bed after the experiment). The maximum uncertainty in the mass balance was estimated to be 10%.

From Table 4 it is also clear that all lignins yield significant amounts of a phenolic bio-oil with the straw-derived lignins showing higher yields when compared to the hardwood derived Alcell (respectively 48–55 wt% versus 39 wt%). Corresponding to the somewhat lower oil yield, Alcell yields more char than the other lignins (43 wt% versus 30–40 wt% for the straw lignins). These results indicate that, apparently, the herbaceous-derived lignins are easier to pyrolyse than the hardwood lignin. The amount of permanent gases is typically 15–20 wt% with approximately equal amounts of CO and CO₂ and less methane.

Fig. 9 compares for each of the lignins the yields of the major detected and identified monomeric phenols, grouped as guaiacols, syringols, alkyl phenols and catechols.

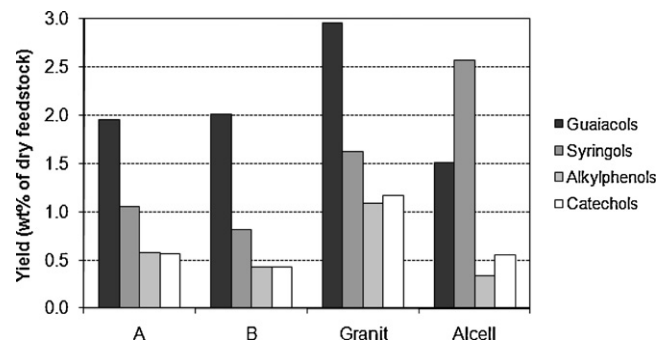


Fig. 9. Identified monomeric phenols from the pyrolysis of the different lignins at 500 °C in a bubbling fluidized bed reactor.

Fig. 9 clearly shows that the composition of the organic phase in the bio-oil is dependent on the biomass type from which the lignin feedstock originated. The herbaceous lignins A, B and Granit produce more guaiacols and less syringols when compared with the hardwood Alcell lignin. Also the amount of alkyl phenols and catechols is higher. The pyrolysis yields for the Granit lignin are higher when compared to the lignins A and B. The reason for this is not clear. Differences in repolymerisation/char formation kinetics can play a role and perhaps the grass-derived lignin that constitutes part of the Granit is easier to crack than the straw-derived lignin. From Fig. 9 it also seems that the ratio guaiacols/syringols is an indicative marker for the source of the lignin. The straws and the Granit lignin show a G/S ratio of around 2 while Alcell yields only a ratio of 0.5, corresponding with higher levels of syringols. These results may be attributed to the chemical nature of the native lignin in the different biomass types and to differences in the pulping method that was applied to produce the lignins.

From Table 4 it can be seen that 4-vinylguaiacol is the major phenolic monomer that is formed during the pyrolysis of the straw/grass lignins in yields from 0.5–1 wt%. For Alcell the predominant phenol is 4-methylsyringol (1.2 wt%). This was also found from the pyrolysis of the beech wood lignin [13].

It is remarkable that pyrolysis of the two reference lignins Granit and Alcell produces a small amount of furfural while this compound is absent in the product slate from the pyrolysis of lignins A and B. Since furfural is a typical degradation product from (hemi) cellulose, its formation indicates the presence of (residual) carbohydrates in the Granit lignin.

Since Alcell contains almost no residual carbohydrates, the formation of furfural from residual (hemi) cellulose is unlikely. Apparently, the furfural is formed from another source, possibly from 'pseudo lignin', a lignin-like substance resulting from polymerization reactions of (hemi)cellulose derivatives like furfural or condensation reactions between lignin and furfural that have been reported to occur during organosolv [9].

When looking at the yields of phenolic substances, it is remarkable that in all four cases the amount of oligomeric substances is approximately 1.6–3.6 times the amount of monomeric phenols (including the unidentified species). This might be attributed to the primary thermal degradation efficiency in the bubbling hot sand bed and/or the occurrence of secondary reactions downstream the reactor bed. A long hot vapor residence time could well enhance the occurrence of secondary repolymerisation reactions that lead to larger fragments. A closer look at the amounts of oligomerics reveals that the herbaceous lignins A, B and Granit produce larger yields when compared to the hardwood Alcell lignin.

Possibly, this is caused by structural differences between the lignins.

The pyrolysis results for the hardwood derived organosolv Alcell lignin are comparable with results that were obtained with

Table 4
Results of the bubbling fluidized bed pyrolysis of four different lignins at 500 °C.

All yields: %, w/w, dry lignin feedstock	Type of lignin feedstock →	Wheat straw organosolv lignin		Wheat straw/grass soda lignin	Hardwood organosolv lignin
	Feedstock code → Products ↓	A	B	Granit	Alcell
Major product fraction	Gas	15.1	17.4	15.2	20.7
	Oil	54.7	51.9	47.6	38.9
	Char	35.6	30.9	39.0	43.0
	Mass balance	105.3	100.2	101.8	102.6
Gases	CO ₂	7.7	9.0	6.2	10.2
	CO	5.8	6.7	6.8	8.1
	CH ₄	1.6	1.7	2.2	2.5
	Total gas	15.1	17.4	15.2	20.7
Water	Water	23.9	19.9	17.1	14.5
Light ends	Acetone	0.30	0.17	BDL	BDL
	Methanol	1.06	0.68	0.99	1.41
	Acetic acid	0.43	0.35	0.31	0.37
	2-Furaldehyde	BDL	BDL	0.10	0.08
	Total light ends	1.8	1.2	1.4	1.9
Guaiacols	2-Methoxyphenol	0.43	0.37	0.73	0.30
	4-Methylguaiacol	0.44	0.45	0.53	0.48
	4-Ethylguaiacol	0.21	0.21	0.43	0.13
	2-Methoxy-4-propyl-phenol	0.03	0.03	0.03	0.03
	Eugenol	0.04	0.04	0.03	0.03
	Isoeugenol	0.19	0.19	0.17	0.14
	2-Methoxy-4-vinyl-phenol	0.52	0.61	0.87	0.18
	Vanillin	0.06	0.08	0.08	0.15
	Aceto-vanillone	0.05	0.05	0.08	0.06
	Total guaiacols	2.0	2.0	3.0	1.5
Syringols	2,6-Dimethoxyphenol	0.39	0.27	0.70	0.73
	4-Methylsyringol	0.41	0.34	0.45	1.21
	4-(2-propenyl)syringone	0.07	0.06	0.07	0.11
	Syringaldehyde	0.06	0.05	0.05	0.40
	Acetosyringone	0.12	0.10	0.36	0.13
	Total syringols	1.1	0.8	1.6	2.6
Alkylphenols	Phenol	0.17	0.13	0.36	0.11
	O-cresol	0.05	0.05	0.10	0.06
	P-cresol	0.16	0.12	0.24	0.10
	M-cresol	0.03	0.03	0.04	0.05
	4-Ethylphenol	0.17	0.10	0.35	0.02
	Total alkylphenols	0.6	0.4	1.1	0.3
Catechols	3-Methoxypyrocatechol	0.16	0.11	0.50	0.30
	Pyrocatechol	0.41	0.32	0.67	0.25
	Total catechols	0.6	0.4	1.2	0.5
Unidentified	Unknowns	3.5	3.0	4.4	3.6
	Monomers (incl. unknowns)	7.8	6.6	11.2	8.5
Undetected	Oligomers	21.4	24.1	18.0	14.0
Total phenolic material	Monomers + oligomers	29.2	30.7	29.2	22.5

BDL, below detection limit.

beech wood derived organosolv lignin [13]. Pyrolysis at 500 °C yielded ~21.5 wt% of phenolic material that contained ~11.6 wt% of monomeric phenols. These yields are in agreement with the yields from the pyrolysis of the Alcell lignin that gave 22.5 wt% of phenolic material with 8.5 wt% of monomeric phenols. At the time (1980!),

these yields were recognized as high for a typical lignin pyrolysis. For example, a recent (2010) fast pyrolysis study of three technical lignins derived from softwood showed only limited yields of bio-oil around 20 wt% containing 60–75% of aromatic species [25]. The lignins were fed as fine powder, using a high velocity jet of nitrogen.

The pyrolysis was conducted at 550 °C in an entrained flow type of reactor.

4. Conclusions

Lignin with a high purity was produced from two wheat straw varieties using ethanol-based organosolv fractionation. Subsequently, these lignins were converted into phenolic oil and biochar by a pyrolysis based lignin biorefinery approach (LIBRA), using bubbling fluidized bed reactor technology. Results indicate that ~80 wt% of the dry lignin can be converted into biochar (30–40%) and bio-oil (40–60%). The bio-oil contains 25–40 wt% (based on the dry lignin weight) of a phenolic fraction constituting of monomeric (7–11%) and oligomeric (14–24%) compounds.

The monomeric phenols consist of guaiacols, syringols, alkyl phenols and catechols. 4-vinylguaiacol is the major phenolic monomer that is formed during the pyrolysis of the straw lignins in yields from 0.5–1 wt%. For the reference lignin Alcell the predominant phenol is 4-methylsyringol (1.2 wt%). The herbaceous lignins A, B and Granit were found to produce more guaiacols, alkyl phenols and catechols and less syringols when compared with the hardwood Alcell lignin. The straws and the Granit lignin show a G/S ratio of around 2 while Alcell yields only a ratio of 0.5, corresponding with higher levels of syringols. These results may be attributed to the chemical nature of the native lignin in the different biomass types.

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